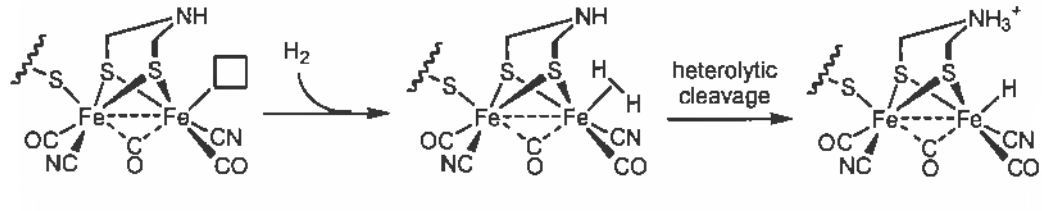
Biologically-Inspired Bimetallic Complexes for the Activation of Small Molecules

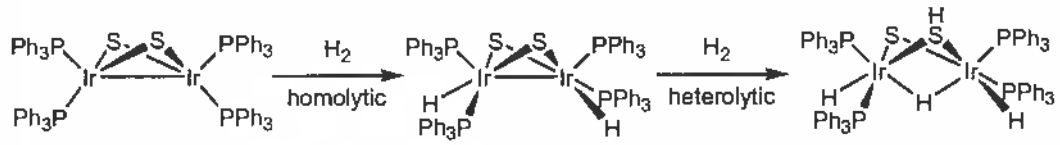
Rachel C. Linck Final Seminar June 7, 2004

Chemists have much to learn from evolutionarily-optimized bioorganometallic enzymes that have developed elegant methods to accomplish some of nature's most important reactions. The interconversion of protons and electrons with dihydrogen gas by hydrogenase enzymes,[1,2] the reduction of nitrogen to ammonia by nitrogenase enzymes,[3,4] and the sequestration of carbon monoxide by carbon monoxide dehydrogenase/acetyl coenzyme A synthase enzymes[5,6] are just a few of the reactions that nature has perfected and chemical industry struggles to achieve with the same efficiency and environmental-friendliness. The production of synthetic models of the active sites of such enzymes may help chemists to understand these processes. This knowledge may aid in the design of efficient catalysts for these industrially-important reactions.

The active site of the iron-only hydrogenase enzymes consists of a diiron center which binds dihydrogen and cleaves it heterolytically, likely through the action of the pendant base in the dithiolate cofactor (Eq 1).[1] The complex $Ir_2(\mu\text{-}S)_2(PPh_3)_4$ reversibly adds one equivalent of dihydrogen homolytically via oxidative addition to produce the iridium(III) dihydride species, $Ir_2(\mu\text{-}S)_2(H)_2(PPh_3)_4$. Upon treatment with another equivalent of dihydrogen, heterolytic cleavage produces the trihydride complex, $Ir_2(\mu\text{-}S)(\mu\text{-}SH)(\mu\text{-}H)(H)_2(PPh_3)_4$ (Eq 2). Isotopic labeling experiments demonstrate that there is no preferred position within $Ir_2(\mu\text{-}S)(\mu\text{-}SH)(\mu\text{-}H)(H)_2(PPh_3)_4$ for H vs. D, and the equilibrium isotope effect is negligible (~ 1).[7]



(1)

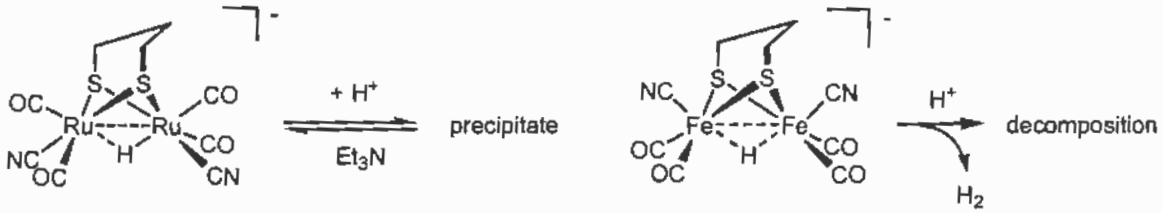


(2)

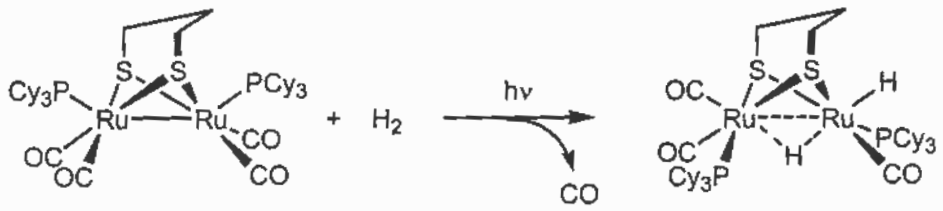
Several synthetic diiron complexes have been prepared to model the active site of the Fe-only hydrogenase enzyme, but no diruthenium systems were previously investigated.[8,9] The dicyanide complex $[Ru_2(S_2C_3H_6)(CN)_2(CO)_4]^{2-}$ reacts with one equivalent of acid to yield $[Ru_2(S_2C_3H_6)(\mu\text{-}H)(CN)_2(CO)_4]^-$, which is much more stable than the diiron analogue.[10] The addition of excess protons to the protonated diruthenium dicyanide complex results in the reversible precipitation of a solid hypothesized to be a proton-bridged dicyanide polymer. The analogous reaction with the diiron dicyanide

complex causes the decomposition of the iron compound to an insoluble black polymer concomitant with the substoichiometric evolution of H_2 (Scheme 1).[11] The increased stability of the diruthenium complexes may lead to better catalysts for the formation of H_2 from protons and electrons.

Scheme 1



The activation of dihydrogen has only been observed indirectly through the photolytically-induced H/D exchange of $[Fe_2(\mu\text{-}H)(SR)_2(CO)_4(PR_3)_2]^+$ Fe-only hydrogenase models with D_2.[10] The diphosphine diruthenium complex $Ru_2(S_2C_3H_6)(CO)_4(PCy_3)_2$ oxidatively adds dihydrogen to produce the dihydride $Ru_2(S_2C_3H_6)(\mu\text{-}H)(H)(CO)_3(PCy_3)_2$, the first example of the homolytic activation of dihydrogen by a synthetic Fe-only hydrogenase model (Eq 3). The protonation of the terminal hydride ligand of $Ru_2(S_2C_3H_6)(\mu\text{-}H)(H)(CO)_3(PCy_3)_2$ has the potential to produce the first synthetic model of the Fe-only hydrogenase enzyme with a bound dihydrogen ligand. While these models are based on diruthenium systems rather than diiron systems, comparison of the iron-based enzyme to synthetic ruthenium mimics may lead to innovations in the preparation of biologically-inspired catalysts.



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